

(12) UK Patent Application (19) GB (11) 2 330 408 (13) A

(43) Date of A Publication 21.04.1999

(21) Application No 9722031.3

(22) Date of Filing 17.10.1997

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(51) INT CL⁶

B07C 5/342 , G01N 21/64

(52) UK CL (Edition Q)

G1A AA6 AG9 AMK AR7 AT23 AT3 AT4
U1S S1253

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US 5329127 A US 4567370 A US 4423814 A

(58) Field of Search

UK CL (Edition P) B6A AK AL ATC , G1A AMG AMHL
AMK
INT CL⁶ B07C 5/34 5/342 , G01N 21/63 21/64
ONLINE: WPI

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(54) Abstract Title

Fluorescent tracers

(57) Fluorescent tracers having known emission characteristics are added to an article so that the article can be identified when illuminated with ultra violet light. The tracers strongly absorb ultra violet radiation but only weakly absorb visible light so that the addition of the tracer does not affect the visual appearance of the article. Specifically the total absorption of each of the tracers in the wavelength range above 390nm does not exceed 10% of the absorption of the tracers in the wavelength range below 390nm.

The tracers are used to allow plastic articles to be recycled with the same combination of tracers being applied to articles made of the same material so that they can be identified and separated from articles made of different material.

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IDENTIFIABLE SUBSTANCES

This invention relates to a substance or composition which can be identified and subsequently sorted, for example for recycling purposes. This
5 invention also relates to a method for identifying the substance and a method for sorting mixed articles for subsequent recycling.

The advantages of recycling substances, for example plastics, have long been known. These include
10 the saving of the earth's resources and the reduction of pollution. However, it is often necessary to provide a way of identifying the substances so that they can be sorted according to, for example, their chemical composition and subsequently recycled. It is
15 known to use fluorescent tracers for this purpose. When use is restricted to single fluorescent tracers, problems may arise from the fact that there are not a lot of suitable ones and the emission spectra of many of them tend to overlap in the limited spectral range
20 available.

US 5201921 discloses a process for identifying plastics by addition of a fluorescent dye. The dyes are coloured and are generally used singly in the plastics material. It is also disclosed that several
25 coloured markers of different wavelengths or intensities can be used. Since high concentrations of the coloured markers can lead to colour distortions, they have to be used in concentrations that are as low as possible, which can make detection difficult.

30 GB-A-2264558 discloses a method of identifying polymer materials. The polymer may be labelled with at least two fluorescent materials capable of fluorescing in the far red or near infrared region, the materials being present in a predetermined weight ratio, whereby
35 the ratio of the fluorescent intensities observed for each material is proportional to the predetermined

weight ratio. Disadvantages of this method are that incorrect signals can be given if either of the tracers age under UV light or at high ambient temperatures, or if the relative emission strengths are affected by the presence of, for example, additives in the polymer.

US 5329127 discloses a method for identifying different plastics which is dependent upon the duration of the fluorescence of the dyes present. This makes identification relatively difficult as sophisticated apparatus is required. In addition, the decay time of the dye may change depending on the plastics environment in which it is used. Furthermore, US 5329127 discloses the use of very coloured dyes in the plastics.

There is therefore a need for an accurate method for the identification of plastics or other materials in which the tracers do not adversely affect the properties, for example the colour, of the materials in which they are included.

In order to solve the problems associated with known methods, the use of one or more fluorescent tracers which allow accurate identification of an identifiable substance and which do not colour the substance is now proposed. A fluorescent tracer is a material which absorbs energy at one wavelength band and emits energy at another (higher) wavelength band. Fluorescent tracers for use in this invention are those which have an absorption which is adequate to give a detectable emission at the higher wavelength. The fluorescent tracers for use in the invention have their characteristic absorption in the UV wavelength range (i.e. below about 390nm) with no substantial absorption in the visible spectrum (which for most people is about 390nm to about 750nm). This ensures that the fluorescent tracer does not appear coloured to the naked eye. The emission wavelength will depend on the

tracer used, but will normally lie in the visible range, or the ir range and is preferably chosen to be greater than 450nm.

Thus, in accordance with a first aspect of this invention, there is provided an identifiable substance comprising a substrate and one or more fluorescent tracers, wherein the total absorption of each of the one or more fluorescent tracers in the wavelength range of 390nm to 750nm is no more than 10% of the total absorption in the wavelength range below 390nm.

Thus, the one or more tracers do not absorb significantly in the visible spectrum and therefore the substance does not appear coloured.

In a preferred embodiment, the total absorption of each of the one or more fluorescent tracers in the wavelength range 390nm to 750nm is no more than 10% of the total absorption in the wavelength range 200nm to 390nm.

Preferably, the total absorption of each of the one or more fluorescent tracers between 390nm and 750nm is less than 5% of the total absorption below 390nm (preferably between 300nm to 390nm, more preferably between 330nm and 390nm) and is even more preferably about 1% of the total absorption below 390nm (preferably between 300nm and 390nm, more preferably between 330nm and 390nm).

When the identifiable substance comprises at least two different fluorescent tracers, the fluorescent tracers preferably have peak emission wavelengths which differ from each other by at least 2nm, even more preferably by at least 5nm.

The identifiable substance is generally a plastics material, for example a thermoplastic material. However, the identifiable substance can be any appropriate material, for example a thermoset, an elastomer, or paper. Particularly preferred are

polymeric materials, for example plastics. The tracers may be admixed with the substrate during its manufacture or can be added to the substance during its conversion into a product, for example a plastics bottle, and can, for example, be printed or painted onto an article made from the substance.

As the total absorption of the one or more fluorescent tracers between 390nm and 750nm is no more than 10% of the absorption below 390nm, it is ensured that the identifiable substance is not coloured at the concentration level used.

The total amount of the fluorescent tracer used in the present invention should be chosen to give an intensity of emission which is detectable by a suitable detector, such as that disclosed in co-pending British Patent Application No. 9722432.1 (Agent's ref. HL56867) but should normally not be used in amounts so high as to give an emission intensity which is detectable by the naked eye under normal natural daylight or synthetic light conditions (such as those prevailing in an artificially lit building), and therefore render an article made from the composition coloured.

Preferably, each tracer is present in an amount by weight of at least 0.01 ppm and preferably no more than about 1000 ppm. Even more preferably, each tracer is present in an amount by weight of at least about 0.1 ppm and preferably no more than about 50 ppm, and even more preferably in an amount by weight of at least 0.5 ppm and preferably no more than about 10ppm.

Typically, the tracers are selected from rare earth complexes of yttrium vanadate (for example complexes of the form YVO_4X , where X is Dy, Eu, Sm, Tb or a combination thereof), ZnS associated to one metal, or other organic or organometallic materials.

Preferably, the tracers are insoluble.

Each tracer is preferably thermally stable up to a

temperature of at least about 350°C. This enables the tracers to be processed with a wide variety of thermoplastics. In addition, it is preferred that the tracers are light-stable as this improves the "shelf life" of the identifiable substance when it is stored, for example, outdoors or under powerful lighting.

The peak emission wavelength of each tracer is preferably greater than 450 nm. This avoids confusion with emissions from other fluorescent materials, such as optical brightening agents which may be present.

The tracers are preferably both chemically and photochemically non-interacting and thereby avoid interference between each other when used in combinations. In addition, in order to comply with food contact regulations when identifiable substances are used to manufacture food packaging, the tracers exhibit low migration into a range of food stimulants, for example aqueous alcohol and acetic acid, and olive oil.

According to a second aspect of the present invention, there is provided a method for identifying a substance comprising the steps of:

(a) adding one or more fluorescent tracers to the substance, wherein the total absorption of each of the one or more fluorescent tracers in the wavelength range between 390nm and 750nm is no more than 10% of the total absorption in the wavelength range below 390nm;

(b) exposing the substance to a radiation source to stimulate fluorescent emission from the tracers; and

(c) detecting the emission wavelengths of the one or more tracers.

This method may also be used for identifying articles made from the substance.

The substance and tracers may exhibit the

preferred properties referred to above. The wavelength of the radiation source is preferably in the range of from 200nm to 390nm and is even more preferably in the range of 330nm to 390nm.

5 An important aspect of this invention is the ability to use a combination of two or more, preferably three or more fluorescent tracers, to mark different substances or compositions to enable automated sorting of articles made from each composition. Thus, a
10 combination of three different tracers, A, B and C, provides a possible 7 different combinations: A alone, B alone, C alone, A + B, A + C, B + C and A + B + C. Seven different compositions could each be marked with one of these combinations, thereby characteristically
15 marking each composition because the emission spectrum (or signature) of each composition will differ. The different tracers used should have peak emissions which are separated by at least 2nm in wavelength, preferably at least 5nm to enable adequate discrimination to be
20 made by a suitable detector such as the detector disclosed in our pending British Patent Application No. (Agent's Ref: HL56867)

 Thus, according to a third aspect of the present invention there is provided a method for sorting mixed
25 articles for recycling, which method comprises the steps of:

 (a) adding a different combination of one or more fluorescent tracers to a substance from which each type of article is made and the same combination
30 of one or more fluorescent tracers to a substance from which the same type of article is made, wherein the total absorption of each of the one or more fluorescent tracers in each article in the wavelength range from 390nm to 750nm is no more
35 than 10% of the total absorption in the wavelength range below 390nm;

- (b) exposing each article to a radiation source;
- (c) detecting the emission wavelengths;
- (d) identifying the type of article; and
- (e) sorting the articles according to the identification in step (d).

Each "type" of article may, for example, be chemically distinct from another "type" of article.

The invention will now be illustrated by reference to the following examples.

Example 1

Using pre-prepared masterbatches, a set of HDPE plaques containing the following tracers (available from Riedel de Haan) was prepared:

CDE 9362 0.5 ppm

CDE 9453 5.0 ppm

CD 340 20 ppm

Each of these tracers has an absorption in the uv range and an emission in the visible range. The total absorption in the visible range (about 390nm to about 750nm) is no more than 10% of the total absorption in the uv range (i.e. wavelength below 390nm).

The masterbatches were prepared as follows: melting high density polyethylene (HDPE), adding an appropriate amount of tracer, blending the mixture in a z-blade mixer, granulating, first passing the granulate through a clean twin-screw compounder and pelletizing the extrudate, and second passing the pelletized extrudate through the compounding extruder and repelletizing.

The masterbatch was diluted with an appropriate amount of virgin HDPE pellets, dry blending by tumbling the mixture, followed by two successive passes through the compounding extruder and pelletizer. The resulting pellets were compression moulded to yield the plaques described above.

The plaques were evaluated alongside a previously

supplied plaque containing all three tracers in combination. The results showed that the emissions of the tracers in combination are essentially additive (that is, equal to the sum of the emissions for the three tracers tested separately) thus confirming that at the low tracer concentrations used, there is no significant interaction. By evaluating samples of the pellets used to mould the above plaques, it was found that the uniformity and homogeneity of the materials were acceptable.

Example 2

A small single head, Hesta extrusion blowmoulding machine equipped with a twin mould was used for the trial. The machine was thoroughly purged with virgin polymer and process conditions stabilised before the trial started. A total of eight runs were made using blends of tracer masterbatches made by the method described in Example 1 and virgin HDPE as indicated in the Table below:

Blends for Blowmoulding Trials:

Key for masterbatches: A = 1000ppm CD340; B = 500ppm CDE9453; C = 50 ppm CDE9362

Run	%A	%B	%C	%HDPE
1	2	0	0	98
2	2	1	0	97
3	0	1	0	99
4	0	1	1	98
5	2	1	1	96
6	2	0	1	97
7	0	0	1	99
8	0	0	0	100

The order of runs was chosen so as to minimise as far as possible the effects of cross-contamination, bearing in mind the relative strengths of the emission signals for the three tracers. When it was deemed
5 necessary, the machine was purged at the end of a run. As soon as it was judged that the extrudate was adequately free of tracers from the preceding run (tested by inspection under a UV lamp), the hopper was emptied and recharged with the next run blend. The
10 blends were made up in 3kg lots for each run. The first few bottles made for each new run were discarded until the process had restabilized with the new blend (again judged by inspection under UV light). At least 200 bottles were collected for each run; these were
15 subsequently labelled with the run number.

The introduction of the tracer masterbatches had no observable effect on the blowmoulding process, and no adjustments to the machine settings were necessary.

A set of the above bottles - labelled only with
20 the run numbers - was provided and the tracer combinations were easily and correctly identified using a fluorosensor. This observation confirms the view that tracer concentrations could be reduced, if required.

CLAIMS

1. An identifiable substance comprising a substrate and one or more fluorescent tracers, wherein the total absorption of each of the one or more
5 fluorescent tracers in the wavelength range between 390nm and 750nm is no more than 10% of the total absorption in the wavelength range below 390nm.

2. An identifiable substance according to claim 1, wherein the total absorption of each of the one or
10 more fluorescent tracers in the wavelength range 390nm to 750nm is no more than 10% of the total absorption in the wavelength range 200nm to 390nm.

3. An identifiable substance according to claim 2, wherein the total absorption of each of the one or
15 more fluorescent tracers in the wavelength range 390nm to 750nm is no more than 10% of the total absorption in the wavelength range 300nm to 390nm.

4. An identifiable substance according to claim 1 or 2, wherein the total absorption of each of the one or
20 or more fluorescent tracers between 390nm and 750nm is about 1% of the total absorption below 390nm.

5. An identifiable substance according to claim 4, wherein the total absorption of each of the one or
25 more fluorescent tracers in the wavelength range 390nm to 750nm is no more than 1% of the total absorption in the wavelength range 200nm to 390nm.

6. An identifiable substance according to claim 5, wherein the total absorption of each of the one or
30 more fluorescent tracers in the wavelength range 390nm to 750nm is no more than 1% of the total absorption in the wavelength range 300nm to 390nm.

7. An identifiable substance according to any preceding claim, comprising at least two different
35 fluorescent tracers, which fluorescent tracers have peak emission wavelengths which differ from each other by at least 2nm.

8. An identifiable substance according to any preceding claim, wherein the substrate is formed of a plastics material.

5 9. An identifiable substance according to any preceding claim, wherein the tracers are selected from rare earth complexes of yttrium vanadate, ZnS associated to one metal, organic materials, or organometallic materials.

10 10. An identifiable substance according to any preceding claim, wherein each tracer is present in an amount of 0.01 ppm to 1000 ppm.

11. An identifiable substance according to any preceding claim, wherein each tracer is thermally stable up to a temperature of at least about 350°C.

15 12. An identifiable substance according to any preceding claim, wherein the peak emission wavelength of each tracer is greater than 450 nm.

20 13. An identifiable substance according to any preceding claim, wherein the tracers are chemically and photochemically non-interacting.

14. An identifiable substance substantially as hereinbefore described with reference to the accompanying examples.

25 15. A method of identifying a substance, which method comprises the steps of:

30 (a) adding one or more fluorescent tracers to the substance, wherein the total absorption of each of the one or more fluorescent tracers in the wavelength range above 390nm is no more than 10% of the total absorption in the wavelength range below 390nm;

(b) exposing the substance to a radiation source to stimulate fluorescent emission from the tracers; and

35 (c) detecting the emission wavelengths of the one or more tracers.

16. A method according to claim 15, wherein the wavelength of the radiation source is preferably in the range 200nm to 390nm.

5 17. A method according to claim 15, wherein the wavelength of the radiation source is preferably in the range 330nm to 390nm.

18. A method for identifying a substance substantially as hereinbefore described, with reference to the accompanying examples.

10 19. A method for sorting mixed articles for recycling, which method comprises the steps of:

(a) adding a different combination of one or more fluorescent tracers to a substance from which each type of article is made and the same combination
15 of one or more fluorescent tracers to a substance from which the same type of article is made, wherein the total absorption of each of the one or more fluorescent tracers in each article in the wavelength range above 390nm is no more than 10%
20 of the total absorption in the wavelength range below 390nm;

(b) exposing each article to a radiation source;
(c) detecting the emission wavelengths;
(d) identifying the type of article; and
25 (e) sorting the articles according to the identification in step (d).

20. A method for sorting mixed articles substantially as hereinbefore described with reference to the accompanying examples.



Application No: GB 9722031.3
Claims searched: 1-19

Examiner: Andrew Bartlett
Date of search: 24 June 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.P): G1A (AMK, AMG, AMHL); B6A (ATC, AK, AL)

Int CI (Ed.6): B07C 5/34 & 5/342; G01N 21/63 & 64

Other: ONLINE:- WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2190996 A (WEST) See whole document	1,15 & 19 at least
X	EP 0466474 A1 (DOWTY SEALS) See whole document	"
X	US 5329127 (BECKER ET AL) See whole document	"
X	US 4567370 (FALLS) See col 3 lines 39-53 in particular	1,15 & 18 at least
X	US 4423814 (WHITE) See whole document	"
X	WO 84/03646 A1 (ANGSTROM ROBOTICS) See whole document	"

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.